J. Chem. Sci. Vol. 127, No. 3, March 2015, pp. 365–374.
DOI 10.1007/s12039-015-0789-y

Synthesis and optical properties of biphenylene ethynylene co-polymers and their model compounds

OKHIL K NAG[a], KAZI M ANIS-UL-HAQUE[a], DIPEN DEBNATH[a], ROCKSHANA BEGUM[a], MUHAMMAD YOUNUS[a,*], NAZIA CHAWDHURY[b], GABRIELE KOCIOK-KÖHN[c] and PAUL R RAITHBY[c]

[a]Department of Chemistry, Shahjalal University of Science and Technology, Sylhet 3114, Bangladesh
[b]Department of Physics, Shahjalal University of Science and Technology, Sylhet 3114, Bangladesh
[c]Department of Chemistry, University of Bath, Bath BA2 7AY, UK
e-mail: myounus_che@yahoo.com; myounus-che@sust.edu

MS received 25 December 2013; revised 20 July 2014; accepted 21 July 2014

Abstract. A new series of biphenylene ethynylene co-polymers, poly(2,5-dialkoxy-4-phenyleneethynylene-4,4-biphenyleneethynylene)s of the general formula [-C≡C-4-C_6H_4-C_6H_4-4-C≡C-C_6H_2(2,5-OR)$_2$-]$_n$ (R = C_4H_9 **P1**, C_8H_{17} **P2**) has been synthesized using a palladium/copper catalyzed coupling reaction between HC≡C-4-C_6H_4-C_6H_4-4-C≡C-H and IC_6H_2(2,5-OR)$_2$I. The new co-polymer [-C≡C-C_6H_2(2,5-OC_8H_{17})$_2$-C≡C-C_6H_2(2,5-OC_4H_9)$_2$-]$_n$ **P5** has also been formed where different alkoxy substituents are present on alternate arene rings in the same polymer backbone. All the polymers were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy and by GPC. The model compounds C_6H_5-4-C_6H_4-C≡C-C_6H_2(2,5-OR)$_2$-4-C_6H_4-C_6H_5 (R = C_4H_9 **M1**, C_8H_{17} **M2**) have also been prepared by the reaction between C_6H_5-4-C_6H_4-C≡CH and IC_6H_2(2,5-OR)$_2$I. Single crystal X-ray structures of **M1**, **M2** and Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$ were determined with a view to obtain a better understanding of the molecular and intermolecular interactions in the solid state which has been used to explain the optical properties of the polymers derived from them. The absorption and photoluminescence spectra of the polymers, **P1**, **P2** and **P5** showed that the lowest energy band is blue shifted due to the introduction of biphenylene fragments into the alkoxy substituted poly(ethynylenephenylene)s.

Keywords. Alkoxy substituted poly(ethynylenephenylene); co-polymer; photoluminescence; sonogashira cross-coupling reaction; x-ray crystallography.

1. Introduction

There has been a growing interest in the synthesis and exploration of the structure-property relationship of π-conjugated polymers (CPs) due to their application in organic electronics[1,2] and fluorescence-based sensing.[3] These polymers have started to find use in making light emitting diodes (LEDs),[4,5] liquid crystals,[6,7] photovoltaic cells,[8] and as sensors for metal ions,[9] warfare agents,[10] bacteria and biomolecules.[3] Since its discovery, extensive studies on the π-conjugated polymers based on polythiophene, poly(*p*-phenylene), poly(phenylenevinylene), polyfluorene and poly(aryleneethynylene) (PAEs) have been performed for their potential applications.[3] PAEs are wide-gap semiconductors which contain a rigid-rod backbone,[11] and can have fluorescence quantum yields of up to unity in solution.[12] Semiconducting nature of PAEs has generated interest in developing electroluminescent polymers for device applications.[13,14] PAEs also have been used to demonstrate in biosensing applications in homogeneous aqueous solution.[15] The water-solubility of PAEs can be achieved by introducing electrolytic functionalities such as quaternary ammonium, sulphonate, carboxylate and phosphonate group into the side chain.[15] However, the widespread uses of PAEs are impaired by synthetic difficulties and poor solubility in common organic solvents that limit their characterizations and applications as active materials in organic electronics. PAEs have been made solution processable by adding alkyl or alkoxy side chains to the aromatic fragment of the polymers so that the optoelectronic properties can be studied either in solution or in spin-cast thin films.[13] Furthermore, it is possible to fine-tune the optoelectronic (HOMO-LUMO energy level) properties, morphology, intra- or inter-chain π-π stacking of the CPs in solid and solution state by adding alkyl or alkoxy side-chain on the polymer

*For correspondence

backbone.[2] Better understanding and optimization of the morphology of CPs in solid or solution state are always important for their proper utilization in applications. Thus, a popular research theme has focused on exploring and tuning properties of the π-conjugated molecules by rational design on the molecular level.

The palladium-catalyzed coupling[16] between terminal acetylenes and aromatic iodides or bromides in amine solvent is the most widely used method for the synthesis of PAEs-type of CPs.[17–21] Alkyne metathesis is recently being used as an efficient synthetic route for the synthesis of high molecular weight polymers.[22] Previously, we reported the synthesis and optical properties of metal-carbon (M-C) σ-bonded transition metal poly(aryleneethynylene)s.[23–26] In this study, we describe the synthesis of soluble alkoxy substituted poly(phenyleneethynylene) homo- and hetero-copolymers with biphenylenes in the rigid-rod backbone. The absorption and photoluminescence spectra of the materials are described and compared with the recently reported (please check section 3.3) alkoxy substituted poly(ethynylenephenylene)s. The molecular structures of the previously reported[27] monomer Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$ and new model compounds **M1** and **M2** are presented. The effect of their twisted conformations in the absorption and photoluminescence spectra of the monomers and polymers is discussed.

2. Experimental

2.1 *Materials and measurements*

Copper(I) iodide, palladium acetate, triphenylphosphine were purchased from Sigma-Aldrich and used as supplied. Ethynylbiphenyl and 4,4-diethynylbiphenyl[27] and 1,4-bis(butyloxy)-2,5-diiodobenzene, 1,4-bis(octyloxy)-2,5-diiodobenzene, 1,4-diethynyl-2,5-bis (butyloxy) benzene and 1,4-diethynyl-2,5-bis(octyloxy) benzene were prepared by literature procedures.[28,29] Solvents were pre-dried from appropriate drying agents and freshly distilled before use.[30]

IR spectra were recorded as CH_2Cl_2 solutions, in a NaCl cell, on Nicolet Nexus FTIR spectrometer. All the NMR samples were prepared as $CDCl_3$ solutions, and standard ^{1}H NMR and ^{13}C {^{1}H} NMR spectra were recorded on Bruker NMR spectrophotometer at 300.22 MHz and 75.50 MHz, respectively. ^{1}H NMR and ^{13}C {^{1}H} NMR were referenced to solvent resonances. EI Mass spectra were recorded on Autospec Mass spectrometer. Microanalyses were performed at the Department of Chemistry, University of Bath, UK. Molecular weight of the polymer was measured by using a Viscotek VE 7510 GPC instrument. A 30 cm long PL gel guard column with 10 microns porosity was used using freshly distilled THF. The flow rate was maintained as 1.0 mL/min. The GPC system was calibrated with polystyrene. Data capture and subsequent data handling was carried out using Viscotek 'Trisec 2000' and 'Trisec 3.0' software.

2.2 *Photoluminescence (PL)*

PL spectra of all the polymers (**P1**–**P5**) were taken in dichloromethane solution of concentration 10^{-4} Mol/dm^3. The photoluminescence spectra of the solutions were measured using a 10 mm quartz cell at room temperature using a Perkin Elmer LS55 Luminescence spectrometer. The spectrometer has a range from 200 nm to 800 nm for excitation. Optical excitation was provided by a Xenon discharge lamp, spectrally resolved by a Monk-Gillieson type monochromator. The PL spectra of polymers **P1** and **P2** and of polymers **P3**–**P5** were taken with excitation from the 350 and 420 nm light beams, respectively. PL spectra of **M1** and **M2** were taken with excitation from the 320 nm line at the second absorption band because excitation at the first absorption band results in saturation in PL signal. The excitation lines were chosen such that the absorption was enough to excite the polymers. The PL signals were passed through a second monochromator and the corrected emission data were collected using a red-sensitive (400–900 nm) R928 photomultiplier.

2.3 *Single crystal X-ray crystallography*

Intensity data were collected at 150 K on a Nonius Kappa CCD equipped with a low temperature device, using graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å) and processed using the Nonius Software.[31] Empirical absorption corrections were applied using the SORTAV program for the Nonius area detector. For structure solution and refinement, the programs SIR-97 and SHELXL-97, and for illustrations, Ortep-3 were employed, respectively.[32–34] The structures were refined by full-matrix least squares, on F^2 and all non-hydrogen atoms were refined with anisotropic displacement parameters; H-atoms were placed in idealized positions and allowed to ride on the relevant carbon atom.

2.4 *Synthesis of the polymers (**P1, P2, P5**)*

All the reactions were performed under nitrogen atmosphere, but no special precautions were taken to exclude oxygen during work-up.

2.4a *Poly[1,4-(4, 4-biphenylethynyl)-2,5-bis(butyloxy)-1,4-phenylene]* ***P1***: Polymer precursors 4,4-biphenylethynylene (0.06 g, 0.29 mmol) and 1,4-bis (butyloxy)-2,5-diiodobenzene (0.14 g, 0.29 mmol) and catalytic amount of $Pd(OAc)_2$ (2 mg), CuI (2 mg) and PPh_3 (4 mg) were added to freshly dried diethylamine (40 mL) in a three-neck flask fitted with a stir bar and reflux condenser under nitrogen atmosphere. The resulting mixture was refluxed for 8 h during the period of time when a fluorescent green-coloured solution was obtained with the precipitation of amine hydrochloride. The solvent was removed under reduced pressure. The residue was dissolved in minimum volume (4 mL) of dichloromethane, and then methanol (60 mL) was added to the solution. A brownish green precipitate was obtained when the solution was allowed to settle at 0°C. The procedure of re-precipitation from dichloromethane/methanol was repeated three times. The product was obtained as a brownish yellow solid in 68% yield (0.08 g). FTIR (CH_2Cl_2, cm^{-1}): 2105 (C≡C), 3301 (C≡CH); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.95 (m, CH_3), 1.50 (m, CH_2), 1.85 (m, CH_2), 3.08 (s, C≡CH), 4.00 (m, OCH_2), 6.86 (s, terminal Ar), 6.98 (s, Ar), 7.25 (s, terminal Ar), 7.54 (m, $C_6H_4C_6H_4$); ^{13}C NMR (76 MHz, $CDCl_3$, δ, ppm): 14.33, 19.75, 31.80 and 69.78 (all-CH_2CH_3), 117.36, 127.25, 127.32, 132.47, 133.04, 133.44, 140.41 and 154.11 (Ar). $M_w = 8310$, $M_n = 2100$, $M_w/M_n = 4$.

2.4b *Poly[1,4-(4,4-biphenylethynyl)-2,5-bis(octyloxy)-1,4-phenylene]* ***P2***: By the application of the procedure of **P1**, utilizing 4,4-biphenylethynylene (0.07 g, 0.35 mmol) and 1,4-bis(octyloxy)-2,5-diiodobenzene (0.20 g , 0.35 mmol) afforded **P2** as yellow solid in 71% yield (0.13 g). FTIR (CH_2Cl_2, cm^{-1}): 2202 (C≡C); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.80 (m, CH_3), 1.25 (m, CH_2), 1.50 (m, CH_2), 1.80 (m, CH_2), 3.95 (m, OCH_2), 6.86 (s, terminal Ar), 6.97 (s, Ar-H), 7.24 (s, terminal Ar), 7.55 (m, $C_6H_4C_6H_4$); ^{13}C NMR (76 MHz, $CDCl_3$, δ, ppm): 14.50, 23.09, 26.52, 29.55, 29.74, 29.78, 29.82, 32.24 and 70.08 (all-CH_2CH_3), 114.45, 127.23, 127.36, 132.49, 133.45, 140.43, 152.29, 154.11 and 154.79 (Ar). $M_w = 13, 200$, $M_n = 5{,}600$, $M_w/M_n = 2.5$.

2.4c *Poly[1,4-bis(ethynyl)-2-5-bis(octyloxy)phenylene-2,5-bis(butoxy)-1,4-phenylene)]* ***P5***: By applying the same synthetic procedure as described for **P1**, using 1,4-bis(ethynyl)-2-5-bis(octyloxy)phenylene (0.05 g, 0.13 mmol) and 1,4-bis(butyloxy)-2,5-diiodobenzene (0.06 g, 0.13 mmol), **P5** was obtained as a brownish-yellow solid in 83% yield (0.06 g). FTIR (CH_2Cl_2, cm^{-1}): 2202 (C≡C); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.80 (m, CH_3), 0.91 (t, CH_3), 1.25 (m, CH_2), 1.52 (m, CH_2), 1.80 (m, CH_2), 3.90 (bs, OCH_2), 6.85 (bs, Ar), 6.95 (s, Ar), 7.24 (s, Ar). $M_w = 9{,}340$, $M_n = 4{,}460$, $M_w/M_n = 2.1$.

2.5 *Synthesis of model compounds (**M1, M2**)*

2.5a *1,4-Bis(4,4-biphenylethynyl)-2,5-bis(butyloxy)benzene* ***M1***: To a solution of 1,4-bis(butyloxy)-2,5-diiodobenzene (0.30 g, 0.68 mmol) in Et_2NH (30 mL) were added 4,4-biphenylethynyl (0.30 g, 1.69 mmol), copper(I) iodide (7 mg), palladium acetate (7 mg) and triphenylphosphine (20 mg), and the resulting mixture was refluxed for 8 h under nitrogen atmosphere. After the completion of the reaction, the solvent was removed under reduced pressure. The crude product was dissolved in minimum volume (3–4 mL) of dichloromethane, and then 50–60 mL methanol was added to the solution. The product was precipitated out which was collected in a sintered crucible in 90% yield (0.35 g). The crystals of the compound were obtained from the recrystallization of the pure product from a dichloromethane/hexane solvent system. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.95 (t, 6H, CH_3), 1.53 (m, 4H, CH_2), 1.58 (m, 4H, CH_2), 4.10 (t, 4H, OCH_2), 6.95 (s, 2H, Ar), 7.29 (t, 2H, Ar), 7.38 (t, 4H, Ar), 7.53 (br-m, 12H, Ar); ^{13}C NMR (76 MHz, $CDCl_3$, δ, ppm): 14.35, 19.70, 31.80 and 69.75 ($OCH_2CH_2CH_2CH_3$), 87.11 and 95.23 (C≡C), 114.41, 117.32, 122.78, 127.42, 128.04, 129.27, 132.39, 140.76, 141.33 and 154.07 (Ar). MS (EI): m/z, 574.3; Anal. Calc. for $C_{42}H_{38}O_2$: C, 87.77, H, 6.66; Found: C, 87.60, H, 6.57%.

2.5b *1, 4-Bis(4, 4-biphenylethynyl)-2,5-bis(octyloxy)benzene* ***M2***: Using the procedures described for **M1**, 1,4-bis(octyloxy)-2,5-diiodobenzene (0.25 g, 0.45 mmol) and 4,4-biphenylethynyl (0.20 g, 1.13 mmol) yielded pale-brown **M2** in 87% (0.27 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.8 (t, 6H, CH_3), 1.22 (m, 12H, $CH_2CH_2CH_2$), 1.45 (m, 8H, CH_2CH_2), 1.85 (m, 4H, CH_2), 1.40 (m, 4H, OCH_2), 6.95 (s, 2H, Ar), 7.30 (t, 2H, Ar), 7.38 (t, 4H, Ar), 7.54 (br-m, 12H, Ar); ^{13}C NMR (76 MHz, $CDCl_3$, δ, ppm): 14.53, 23.11, 26.52, 29.75, 29.80, 29.83, 32.25 and 70.06 (all-CH_2), 87.12, 95.24 (C≡C), 114.40, 117.31, 122.78, 127.40, 129.27, 132.41, 133.36, 140.77, 141.34, and 154.07 (Ar); MS (EI): m/z, 686.6; Anal. Calc. for $C_{42}H_{38}O_2$: C, 87.42, H, 7.92; Found: C, 87.30, H, 7.68 %.

3. Results and Discussion

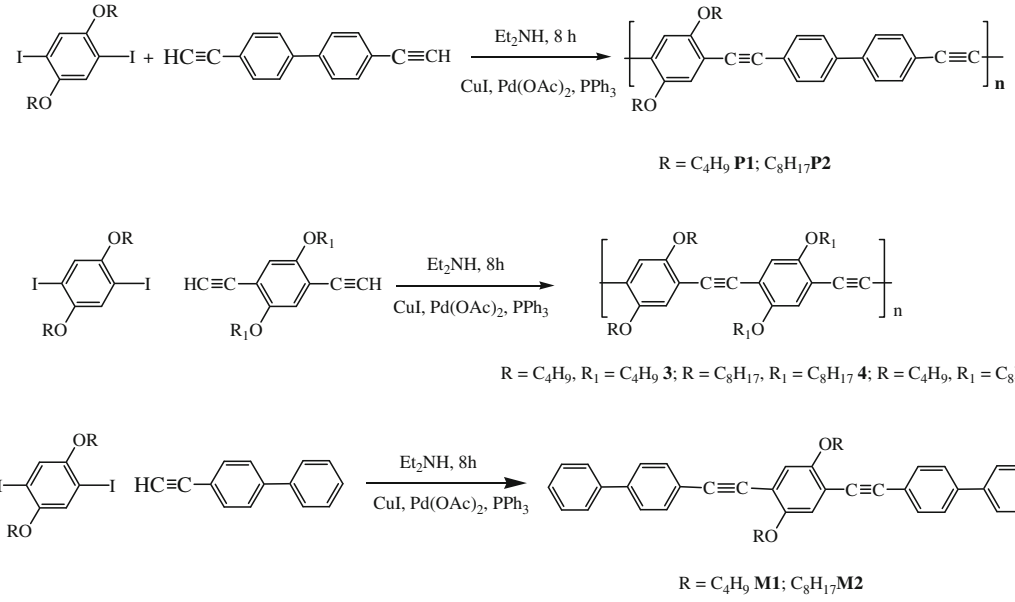
3.1 *Synthesis and characterization of polymers and model compounds*

The new alkoxy ethynyl polymers and their molecular precursors were prepared using a Sonogashira cross-coupling reaction[21] as illustrated in scheme 1. Equimolar quantity of 1,4-bis(butyloxy)-2,5-diiodobenzene and 4,4-diethynylbiphenyl were reacted in the presence of catalytic amounts of $Pd(OAc)_2$, CuI and PPh_3, in diethylamine, at 55°C, for 8h to afford expected co-polymer **P1**. The polymer was isolated as brownish-yellow solid in 68% yield after repeated precipitation from CH_2Cl_2 by methanol. Polymers **P2, P3, P4** and **P5** were prepared similarly using equimolar quantities of aryl diiodides and diethynyl aryl compounds. The homo-polymer **P3** and **P4** have been reported previously using a different route involving reactions of tributyl tin reagents which gives higher molecular weight.[35] The co-polymer **P5** represents a new class of co-polymer in which alternate arene rings in the polymer chain have different alkoxy substituents. The model compounds **M1** and **M2** were formed similarly, but using 2.5 equivalents of mono-terminal ethynylbiphenyl instead of di-terminal 4, 4-diethynylbiphenyl.

The polymers and model molecular compounds are moderately soluble in dichloromethane, chloroform and THF. The solubility of octyloxy substituted polymers is much higher than the corresponding butyloxy substituted polymers. All the polymers are air stable. The molecular weights were determined by gel permeation chromatography (GPC), and the number average molecular weights of **P1, P2, P3**, **P4** and **P5** are 2100, 5260, 3130, 4840 and 9340, respectively. The molecular weights of the polymers, especially for **P1** and **P3** appeared to be very low, but they have substantial differences between their molecular weight distributions. The weight average molecular weights (M_w), number average molecular weights (M_n) and molecular weight distribution values of the polymers are shown in table 1.

The molecular compounds were characterized initially by ^{1}H NMR and ^{13}C NMR spectroscopy. In **M1**, the aliphatic protons of the methyl and methylene groups bonded to oxygen displayed triplets at $\delta = 0.95$ and 4.10 ppm, respectively; and the other CH_2 groups appeared as multiplets at $\delta = 1.50$, 1.75 and 1.85 ppm. The aromatic protons of the arene rings bonded to the alkoxy groups were detected at δ 6.95 ppm as a singlet. In the ^{13}C NMR spectrum of **M1**, the carbon belonging to butoxy side chain gave signals at δ =14.35, 19.70, 31.80 and 69.75 ppm, and the carbons belonging to ethynyl groups were observed at $\delta = 87.11$ and 95.23 ppm, and the signals at $\delta = 114.41$, 117.32, 122.78, 127.42, 128.04, 129.27, 132.39, 140.76, 141.33 and 154.07 ppm were assigned to aromatic carbons. Compound **M2** displayed similar spectral pattern in its ^{1}H and ^{13}C NMR spectra.

For **P1**, the presence of ethynyl fragments in the polymer backbone was confirmed by the IR stretching frequency at 2105 cm^{-1}. In addition, an IR stretching frequency at 3301 cm^{-1} showed the presence of terminal acetylene group suggesting the lower molecular weight of the polymer. For polymer **P2**, υ(C≡C) was observed at 2202 cm^{-1}, but no peak for terminal acetylenic hydrogen was seen in the 3300 cm^{-1} region



Scheme 1. Synthesis of poly(2,5-dialkoxy-1,4-phenylene-4,4-biphenyleneethynylene)s and their model compounds.

Table 1. Molecular weights and absorption and photoluminescence spectral data of the polymers (**P1**-**P5**) and the model compounds (**M1, M2**)

Compounds	[a]M.p.(°C)	[b]M_w	[c]M_n	M_w/M_n	[d]λ (nm)	[e]λ (nm)	[f]Log ε
P1	181*	8310	2100	4	385	466	4.48
P2	190	13200	5260	2.5	390	463	5.25
P3	170*	8770	3130	2.8	433	514	4.63
P4	161	10400	4840	2.2	436	490, 511	4.60
P5	140	9340	4460	2.1	437	510	4.77
M1	-	-	-	-	378	433	0.97
M2	-	-	-	-	370	437	0.11

[a]Melting point, *Decomposition point, [b]Weight average molecular weight, [c]Number average molecular weight, [d]Absorption maximum wavelength, [e]Emission maximum wavelength, [f]Logarithm of absorption co-efficient (M^{-1} cm^{-1}).

demonstrating the formation higher molecular weight polymer as evident by the GPC. Similarly, for **P3**, **P4** and **P5**, υ(C≡C) were observed at 2197, 2202 and 2202 cm^{-1}, respectively. As expected, for lower molecular weight polymer **P3**, υ (≡C-H) was observed at 3301 cm^{-1} indicating the ethynyl group as terminal end group of the polymer.

The characterization of the polymers was also possible from analysis of the ^{1}H NMR spectra, however, the ^{13}C NMR spectra of the polymers failed to show all the signals for the carbon skeleton especially in the aromatic region. This can be attributed to the lower solubility of the polymers. For polymer **P1**, the butoxy protons -CH_3, -CH_2, -CH_2 and O-CH_2 displayed signals as multiplets and broad triplet at $\delta = 0.95, 1.50, 1.85, 4.00$ ppm, respectively. The terminal ethynyl protons were detected at $\delta = 3.1$ ppm indicating the presence of terminal acetylene as end groups in the polymer. In the aromatic region of polymer **P1**, three singlets $\delta = 6.86$, 6.98 and 7.25 ppm were observed. Among them, signals at 6.86 and 7.25 ppm were characterized for the two protons of the terminal iodine substituted butyloxy aryl fragments, and signal at 6.98 ppm was characterized for the protons of butyloxy aryl fragments in the polymer core. Polymer **P2** and **P5** also give ^{1}H NMR signals in the expected aliphatic and aromatic region. The nature of the known polymers **P3** and **P4** was confirmed by comparison of the spectroscopic data with the previously published results.[35]

3.2 *Crystal structure determinations of model compounds*

The crystal structures of **M1** (CCDC-997486), **M2** (CCDC-997487) and Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$ (CCDC-997488) have been determined using single crystal X-ray diffraction techniques in order to study the ring conformations along the molecular chains in the model compounds, so that these can be related to the conformations in the polymers. Potentially, the most significant structural feature is the twist, or dihedral angle between the two adjacent arene rings in the biphenyl units, as this may influence the extent of the π overlap along the chains. There is essentially free rotation about the alkynyl C≡C triple bonds so that the orientation of the biphenyl units with respect to the central alkoxy-substituted arene ring should have less significance.

The molecular structure of **M1** is shown in figure 1, and confirms the spectroscopic assignments, with the OC_4H_9 chains at the 2 and 5 positions. The bond parameters within the molecule do not deviate significantly from expected values, and the alkynyl units are essentially linear {C(13)-C(15)-C(16), 179.7(3)°; C(15)-C(16)-C(17), 177.3(2)°; C(10)-C(29)-C(30), 179.0(2)°, C(29)-C(30)-C(31), 178.0(2)°}. Of interest is the dihedral angle of only 2.3° between the arene rings C(17)C(18)C(19)C(20)C(27)C(28) and C(21)C(22)C(23)C(24)C(25)C(26) and of only 1.1° between rings C(31)C(32)C(33)C(34)C(41)C(42) and C(35)C(36)C(37)C(38)C(39)C(40). The inner arene rings of the two biphenyl groups make angles of 29.0°{C(17)C(18)C(19)C(20)C(27)C(28)} and 29.3° {C(31)C(32)C(33)C(34)C(41)C(42)} with the alkoxy-substituted central arene ring {C(9)C(10)C(11)C(12) C(13)C(14)], respectively. An examination of the crystal packing shows no evidence of $\pi - \pi$ stacking and there are no hydrogen bond interactions present.

Similarly, an examination of the crystal packing in the structure of **M2** provides no evidence of hydrogen bonding interactions or $\pi - \pi$ stacking. However, there is greater evidence of inter-digitation between the longer OC_8H_{17} chains between adjacent molecules. The molecular structure of **M2** is illustrated in figure 2. The molecule sits on a crystallographic centre

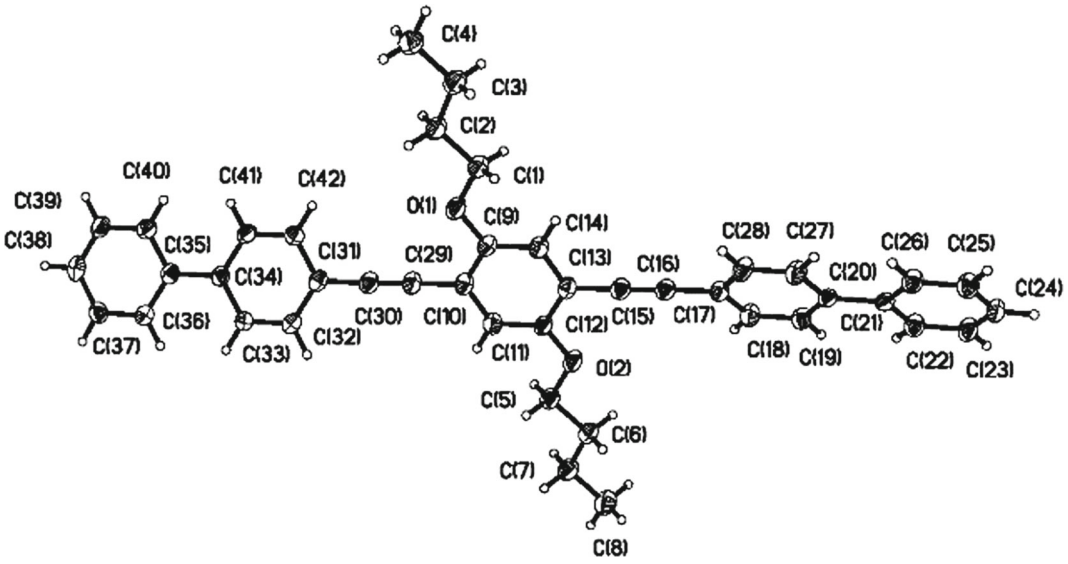


Figure 1. The molecular structure of C_6H_5-4-C_6H_4-C≡C-C_6 H_4(2,5-$OC_4H_9)_2$-C_6H_4-4-C_6 H_5 **M1** showing the atom numbering scheme adopted. The atomic displacement ellipsoids are drawn at the 50% level.

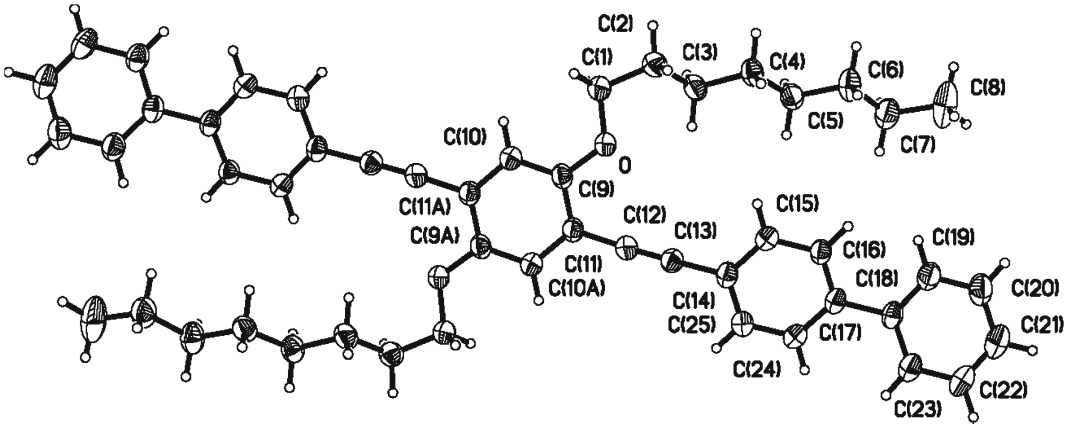


Figure 2. The molecular structure of C_6H_5-4-C_6H_4-C≡C-C_6H_4(2,5-$OC_8H_{17})_2$-C_6H_4-4-C_6H_5 **M2** showing the atom numbering scheme adopted. The atomic displacement ellipsoids are drawn at the 50% level.

of symmetry positioned at the centroid of the central arene ring and, therefore, the asymmetric unit contains half a molecule. As for **M1**, the bond parameters in the structure of **M2** are unremarkable, and the alkynyl groups are essentially linear {C(11)-C(12)-C(13), 177.1(3)°; C(12)-C(13)-C(14), 178.9(3)°}. However, in contrast to **M1**, in **M2** the dihedral angle between the rings of the independent biphenyl group is 29.2°, and the angle between the inner biphenyl ring {C(14)C(15)C(16)C(17)C(24)C(25)} and the central alkoxy-substituted arene ring {C(9)C(10)C(11)C(9A)C(10A)C(11A)} is 9.4°. Thus, the relative orientations of the ring systems in **M1** and **M2** are significantly different in the solid state.

The dihedral angles in **M1** and **M2** may be compared with those observed in Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$, the structure of which was determined as part of the overall project, and with other molecules, whose structures have been reported in the literature, that contain the C≡C-4-C_6H_4-C_6H_4-4-C≡C unit.[36,37] Molecules of Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$ crystallize in the triclinic space group *P-1* (no. 2) with two independent, but structurally similar, molecules in the asymmetric unit. There are no significant intermolecular interactions present in the crystal lattice. The molecular structure of one of two independent molecules is shown in figure 3, and the dihedral angle between the

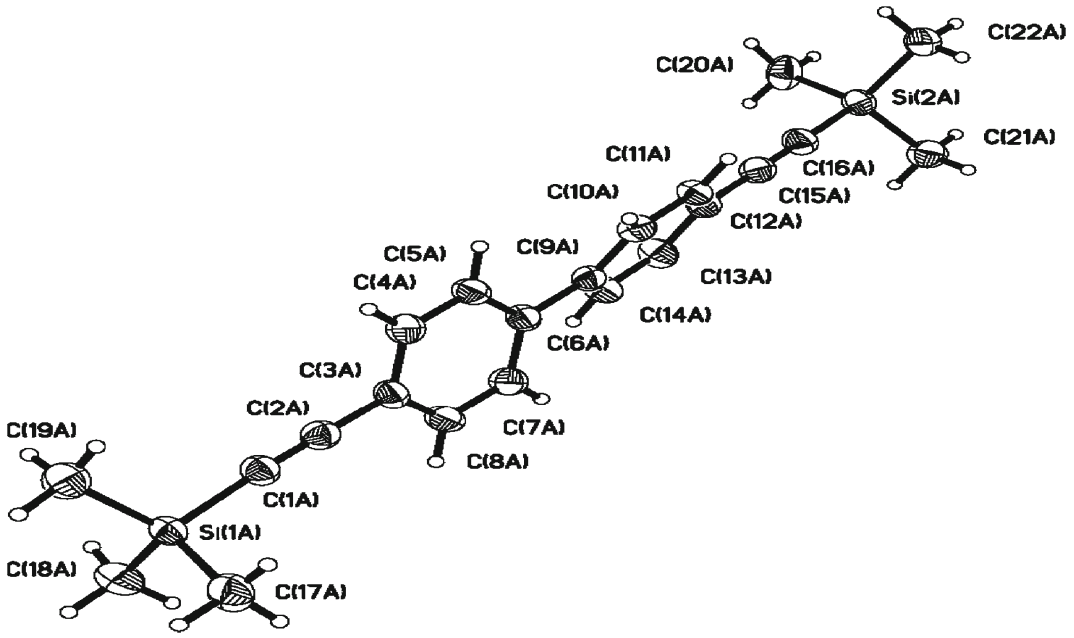


Figure 3. The molecular structure of one of the two independent molecules of Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$ showing the atom numbering scheme adopted. The atomic displacement ellipsoids are drawn at the 50% level.

arene rings {C(3A)C(4A)C(5A)C(6A)C(7A)C(8A)} and {C(9A)C(10A)C(11A)C(12A)C(13A)C(14A) is 32.1°(32.9° in the second molecule). This compares well with the value of 29.2° observed in **M2**. Of the other structures in the Cambridge Structural Database[38] that contain the C≡C-4-C_6H_4-C_6H_4-4-C≡C the dihedral angles between the two arene ring range from 0.0°(constrained by crystal symmetry) to 29.6°.[36,37] Therefore, the values for the dihedral angle found in the solid state structures of **M1** and **M2** are in the expected range, although **M1**, with dihedral angles of 1.1 and 2.3°, displays the smallest dihedral angle in any reported system where crystallographic symmetry is not imposed on the orientation. The deviation from planarity is related to the reduction of the steric interactions between the ring hydrogen atoms on the adjacent ring systems, and these distortions (maximum *ca.* 30°) have a significant influence on the delocalization along the molecular chains.

3.3 *Optical spectroscopy (absorption and photoluminescence) of the polymers and model monomers*

Figure 4a–d shows the absorption and photoluminescence spectra of the model compounds **M1** and **M2**, and polymers **P1-P5** measured in dichloromethane solution, at room temperature. In contrast to the unsubstituted 1,4-bis(phenyleneethynylene)benzene where one broad absorption band was observed in the spectral region 250–350 nm,[39] the alkoxy substituted model compounds **M1** and **M2** displayed two peaks of almost equal intensity centered at 320 and 360 nm (figure 4a). Alkoxy substitutents in **M1** and **M2** modify the central arene ring π-orbitals through resonance interaction with oxygen lone pairs. This leads to the developments of two HOMO orbitals, HOMO-1 and HOMO-2, and electronic transition from these orbitals to the LUMO resulted two separate bands.[40] These principal bands are associated with the rigid-rod backbone of the molecules.[35] Similar spectral features were reported by Li *et al.* for alkoxy substituted PPEs.[12]

All the relevant spectral parameters are summarized in table 1. Two separate spectral patterns were observed in the absorption spectra for the two different sets of polymers (figure 4b). The first set, **P1** and **P2**, contain biphenylene fragments that alternate with the ethynyl alkoxy phenylene units in the polymer. In contrast, the second set **P3**, **P4** and **P5** are homopolymers that have only ethynyl alkoxy phenylenes as repeating unit. The spectra of **P3**, **P4** and **P5** consist of three bands in the measured spectral range. The first absorption band is centred at 437 nm, the second band is centred at 310 nm and a third is a shoulder centred at 225 nm. The lowest energy band of the co-polymers **P1** and **P2** was observed at 387 nm which is blue shifted by 50 nm with respect to the homopolymer **P3**, **P4** and **P5** (figure 4b). The shift of absorption bands from monophenyl to biphenyl in the polymer backbone can be explained by analyzing the molecular structure of

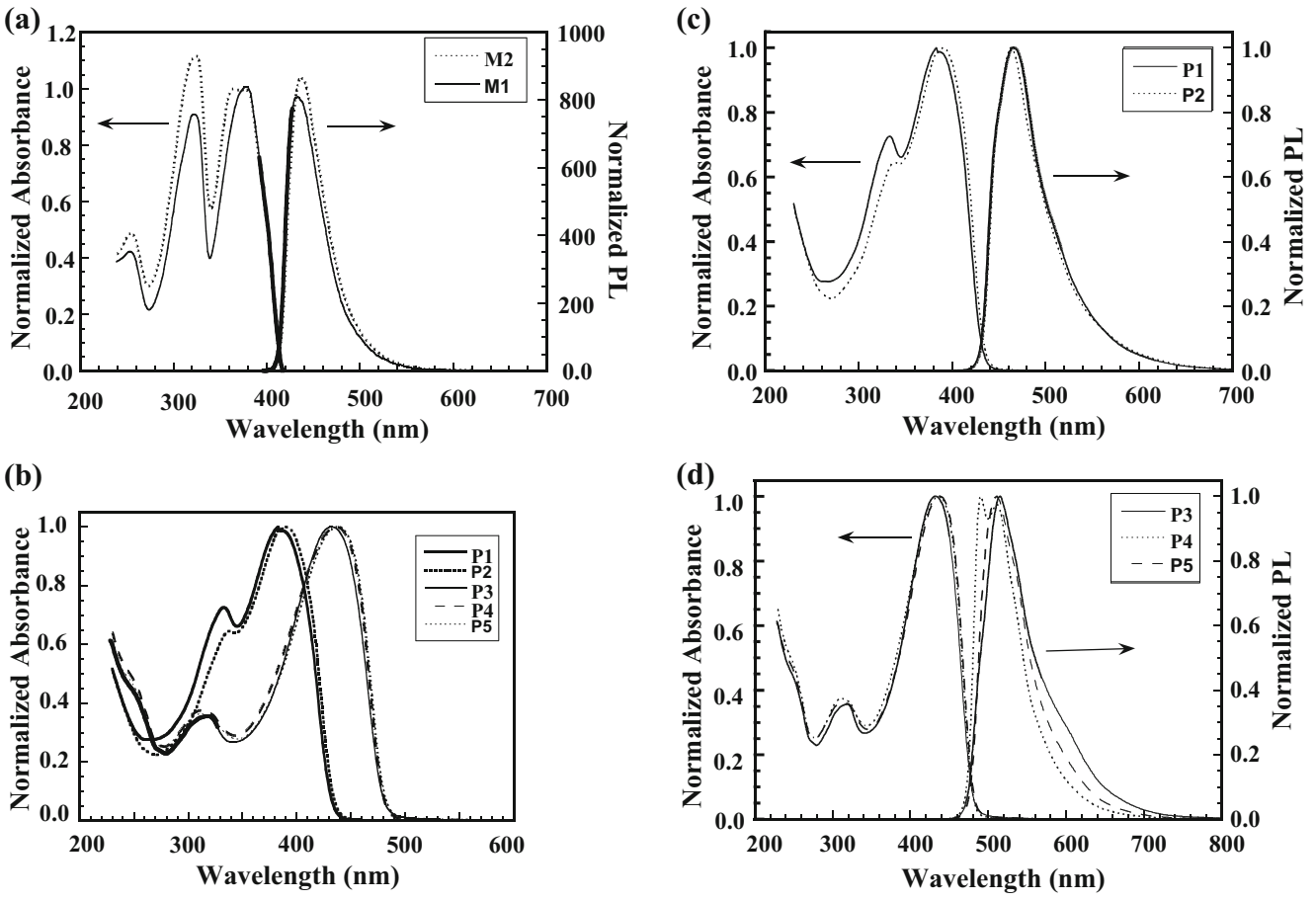


Figure 4. (**a**) The solution absorption and photoluminescence spectra of the model compounds **M1** and **M2**; (**b**) The solution absorption spectra for the polymers **P1** – **P5**; (**c**) The absorption and photoluminescence spectra of the polymers **P1** and **P2** recorded at room temperature; (**d**) The absorption and photoluminescence spectra of the polymers **P3** – **P5** recorded at room temperature.

the building block Me_3Si-C≡C-4-C_6H_4-C_6H_4-4-C≡C-$SiMe_3$. The dihedral angle (torsion angle) between the two phenyl rings is 32.1°. This deviation of the planarity in the phenyl rings of the polymers reduced conjugation among the polymer backbone causing the blue shift in the lowest absorption bands.[40] Similar blue shift of the lowest absorption bands were observed in case of the alkoxy substituted co-polymers where every second benzene rings are unsubstituted in the polymers.[12] No significant effect of the chain length of the alkoxy group was observed in the UV spectra of the polymers described here or in related systems.[41]

Photoluminescence (PL) measurements were carried out on the materials in order to establish their luminescent properties to assess their potential into electro-optic devices. Figure 4a shows the absorption and PL of **M1** and **M2**. Both materials show an emission band centred at around 435 nm. Figure 4c and 4d show the room temperature photoluminescence spectra of the polymers. The photoluminescence (PL) spectra of all the polymers display one emission band peaking at 475–510 nm range. The small energy shift (Stokes shift) between absorption and emission bands confirmed that the origin of emission is singlet excited state. Recent study on the alkoxy molecular system suggests that the excited state geometry of the phenylethynyls is more planar compared to the ground state indicating the presence of single emitting species.[40] Similar emission spectra have been observed by other groups.[35] No emission from triplet excited state was observed. However, it is expected that the triplet state will be at a constant separation of 0.7 ± 0.1 eV below the first singlet state.[42] The evolution of the first triplet excited state in an extensive series of platinum containing phenyleneethynylene monomers and polymers and in an analogous series of all-organic polymers where the platinum fragments is replaced by a phenylene group has been studied.[42] Introduction of a heavy metal such as platinum in the main chain of these polymers can induce spin-orbit coupling, and emission from the

triplet state (phosphorescence) can be easily detected, but only at low temperatures in the solid state.[43]

4. Conclusions

Using a palladium/copper catalyzed coupling reaction a new series of co-polymers poly(2,5-dialkoxy-4-phenyleneethynylene-4,4-biphenyleneethynylene)s of the general formula [-C≡C-4-C_6H_4-C_6H_4-4-C≡C-C_6H_4(2,5-OR)$_2$-]$_n$ (R = C_4H_9 **P1**, C_8H_{17} **P2**) have been synthesized. In addition, the new co-polymer [-C≡C-C_6H_4(2,5-OC_8H_{17})$_2$-C≡C-C_6H_4(2,5-OC_4H_9)$_2$-]$_n$ **P5** has been prepared where different alkoxy substituents are attached to alternate arene rings along the polymer backbone. The absorption and photoluminescence spectra of the polymers, **P1** and **P2** confirmed that the lowest energy band is blue shifted by the introduction of the biphenylene groups into the alkoxy-substituted poly(ethynylenephenylene)s. The blue shift of the lowest energy band was a consequence of the loss of planarity that was evident in the X-ray structure of the model compounds.

Supplementary Information

The ^{13}C NMR spectrum of C_6H_5-4-C_6H_4-C≡C-C_6H_4(2,5-OC_8H_{17})$_2$-C_6H_4-4-C_6H_5 M2; and crystal data, data collection and structure refinement for **M1**, **M2** and $Me_3SiC{\equiv}C(C_6H_4)_2C{\equiv}CSiMe_3$ are available from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. The CCDC reference numbers for the three crystal structures are 997486-997488. Supplementary information is also available at www.ias.ac.in/chemsci.

Acknowledgements

We are grateful to the Leverhulme Trust and the Royal Society, UK; and Higher Education Quality Enhancement Project (HEQEP), UGC, Bangladesh for financial support (to M. Y.), Shahjalal University for study leave (to M. Y.), and the EPSRC for funding to purchase the X-ray diffractometer. The EPSRC sponsored polymer molecular weight determination service run by RAPRA is gratefully acknowledged.

References

1. Pei Q B, Yu G, Zhang C Z, Yang Y and Heeger A 1995 *Science* **269** 1086
2. Gunes S, Neugebaur H and Sariciftci N S 2007 *Chem. Rev.* **107** 1324
3. Thomas I S W, Joly G D and Swager T M 2007 *Chem. Rev*. **107** 1339
4. Mitscheke U and Bauerle P 2000 *J. Mater. Chem.* **10** 1471
5. Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackay K, Friend R H, Burn P L and Holmes A B H 1990 *Nature* **347** 539
6. Pang Y, Li J, Jones D, Claridge J B, Loye H C Z and Bunz U H F 1999 *Macromolecules* **32** 4460
7. Zhu Z and Swager M 2002 *J. Am. Chem. Soc.* **124** 9670
8. Coakley K M and Mcgehee M D 2004 *Chem. Mater*. **16** 4533
9. Kim J, McQuade D T, McHugh S K and Swager T M 2000 *Angew. Chem. Int. Ed*. **39** 3868
10. Zhang S-W and Swager T M 2003 *J. Am. Chem. Soc.* **125** 3420
11. Bunz U H F 2000 *Chem. Rev.* **100** 1605
12. Li H, Powell D R, Hayashi R K and West R 1998 *Macromolecules* **31** 52
13. Ofer D, Swager T M and Wrighton M S 1995 *Chem. Mater.* **7** 418
14. Pschirer N G, Miteva T, Evans U, Roberts R S, Marshall A R, Neher D, Myrick M L and Bunz U H F 2001 *Chem. Mater.***13** 2691
15. Bunz U H F 2009 *Macromol. Rapid Commun.* **30** 772
16. Sonogashira K 2002 *J. Organomet. Chem.* **653** 46
17. Yamamoto T, Fang Q and Morikita T2003 *Macromolecules* **36** 4262
18. Bangcuyo C G, Rampey-Vaughn M E, Quan L T, Angel S M, Smith M D and Bunz U H F 2002 *Macromolecules* **35** 1563
19. Weder C and Wrington M S 1996 *Macromolecules* **29** 5157
20. Moroni M, Moigne J L and Luzzati S 1994 *Macromolecules* **27** 562
21. Rattanatraicharoen P, Yamabuki K, Oishi T and Onimura K 2012 *Polym. J.* **44** 224
22. Bunz U H F 2001 *Acc. Chem. Res*. **34** 998
23. Younus M, Köhler A, Cron S, Chawdhury N, Al-Mandhary M R A, Lewis J, Long N J, Friend R H and Raithby P R 1998 *Angew. Chem. Int. Ed*. **37** 3036
24. Chawdhury N, Köhler A K, Friend R H, Younus M, Long N J, Raithby P R and Lewis J 1998 *Macromolecules* **31** 722
25. Long N J, White A J P, Williams D J and Younus M 2002 *J. Organomet. Chem.* **649** 94
26. Saha R, Qaium M A, Debnath D, Younus M, Chawdhury N, Sultana N, Kociok-Kohn G, Ooi L and Raithby P R 2005 *Dalton Trans.* 2760
27. Takahashi S, Kuroyama Y, Sonogahara K and Hagihara N 1980 *Synthesis* 627
28. Antonelli E, Rosi P, Sterzo C L and Viola E 1999 *J. Organomet. Chem.* **578** 210
29. Bao Z, Chen Y, Cai R and Yu L 1993 *Macromolecules* **26** 5281
30. Errington R J 1997 In *Advanced Practical Inorganic and Metalorganic Chemistry* (London: Chapman and Hall)
31. Otwinowski Z and Minor W 1999 In *DENZO-SMN Manual* (Dallas: University of Texas Southwestern Medical Center)

32. Altomare A, Burla M C, Camalli M, Cascarano G L, Giacovazzo C, Guagliardi A, Moliterni A G G, Polidori G and Spagna R 1999 *J. Appl. Cryst.* **32** 115
33. Sheldrick G M 1997 *SHELXL 97 Program for Crystal Structure Determination*, (Germany: Universität Göttingen)
34. Farrugia L J 1997 *J. Appl. Cryst.* **30** 565
35. Pizzoferrato R, Berliocchi M, Di Carlo A, Lugli P, Venanzi M, Micozzi A, Ricci A and Lo Sterzo C 2003 *Macromolecules* **36** 2215
36. Perera K P U, Krawiec M and Smith D W 2002 *Tetrahedron* **58** 10197
37. Perera K P U, Abboud K A, Smith D W and Krawiec M 2003 *Acta Cryst. C* **59** 107
38. Allen F H 2002 *Acta Cryst. Sec B* **58** 380
39. Levitus M, Schmieder K, Ricks H, Shimizu K D, Bunz U H F and Garcia-Garibay M A 2001 *J. Am. Chem. Soc.* **123** 4259
40. James P V, Sudeep P K, Suresh C H and Thomas K G 2006 *J. Phys. Chem. A* **110** 4329
41. Francke V, Mangel T and Mullen K 1998 *Macromolecules* **31** 2447
42. Köhler A, Wilson J S, Friend R H, Al-Suti M K, Khan M S, Gerhard A and Bassler H 2002 *J. Chem. Phys.* **116** 9457
43. Chawdhury N, Köhler A K, Friend R H, Wong W-Y, Lewis J, Younus M, Raithby P R, Corcoran T C, Al-Mandhary M R A and Khan M S 1999 *J. Chem. Phys.* **110** 4963